

Preliminary investigation of mixed adsorbents for the removal of copper and methylene blue from aqueous solutions

Albadarin, A., Mo, J., Glocheux, Y., Allen, S., Walker, G., & Mangwandi, C. (2014). Preliminary investigation of mixed adsorbents for the removal of copper and methylene blue from aqueous solutions. *Chemical Engineering Journal*, 255, 525. <https://doi.org/10.1016/j.cej.2014.06.029>

Published in:
Chemical Engineering Journal

Document Version:
Early version, also known as pre-print

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Manuscript Number: CEJ-D-14-01907R1

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Article Type: Research Paper

Keywords: Multi-adsorbents; Wastewater; Adsorption technique; Heavy metals; Dyes

Corresponding Author: Dr. Ahmad B. Albadarin, Ph.D

Corresponding Author's Institution: University of Limerick

First Author: Ahmad B. Albadarin, Ph.D

Order of Authors: Ahmad B. Albadarin, Ph.D; Jiabin Mo, MSc; Yoann Glocheux, PhD; Gavin walker, PhD; Stephen Allen, PhD; Chirangano Mangwandi, PhD

Abstract: With most recent studies being focused on the development of advanced chemical adsorbents, this paper investigates the possibility of using two natural low-cost materials for selective adsorption. Multi-adsorbent systems containing tea waste (TW) and dolomite (DO) have been tested for their effectiveness in the removal of copper and methylene blue from aqueous solutions. The effects of contact time, solution pH and adsorption isotherms on the sorption behaviour were investigated. The Langmuir and Freundlich isotherms adequately described the adsorption of copper ions and methylene blue by both materials in different systems. The highest adsorption capacities for Cu and MB were calculated as 237.7 mg/g at pH 4.5 and 150.4 mg/g at pH 7 for DO and TW:DO respectively. Tea waste and dolomite were characterized by Fourier transform infrared spectroscopy, scanning electron microscopy and Energy dispersive X-ray analysis. The removal of Cu and MB by dolomite was mainly via surface complexation while physisorption was responsible for most of the Cu and MB adsorption onto tea waste. Identifying the fundamental mechanisms and behaviour is key to the development of practical multi-adsorbent packed columns.

Response to Reviewers: RESPONSE TO REVIEWERS:

Authors would like to thank the reviewers for very constructive comments. We believe that addressing the reviewer's concerns has led to improvements in the manuscript.

The following explains how we handled the comments raised by reviewers.

Response to Reviewer No 1:

It is a very good study which aims the investigation of adsorption/removal of a heavy metal (copper) and a dye (methylene blue) using low-cost adsorbent. My comments are listed below.

1. Fig.1 presents the kinetic data without fitting, while Fig.2 after fitting. I recommend authors to move Fig.1 to Supporting information section.

Answer: Figure 1 has been moved to the Supplementary data as recommended.

2. Fig. 4 has 6 sub-figs without numbering. But, I think they need merging into at least 2 sub-figs and not 6.

Answer: Putting these figures in 2 sub-figures will not allow clear demonstration of the data and isotherm fitting. However, Figure 4 was split into 2 figures.

3. The major absorbencies (as described in text) should be illustrated in Fig. 6, 7 (FTIR).

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4. It will be good to add a column in Table 1 (for each fitting), presenting the %change between $Q_{e,exp}$ and $Q_{e,cal}$.

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5. Authors should illustrate (as scheme/figure) an adsorption mechanism based on their findings (FTIR, etc). It is more attractive for any reader to read and follow a figure than only text.

Answer: A new figure (Figure 6) has been added. The figure illustrates the possible removal mechanisms for copper and methylene blue onto dolomite and tea waste.

Response to Reviewer No 2:

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Page 6: row 129 "The Cr(VI)percentage removal...". It should be Cu(II).

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Answer: The manuscript was revised and all typo mistakes have been corrected.

Dear Editor,

On behalf of myself and my colleagues (co-authors of this work), please find attached an electronic copy of the manuscript "*Preliminary investigation of mixed adsorbents for the removal of copper and methylene blue from aqueous solutions*" submitted to "**Chemical Engineering Journal**" for possible publication.

This work is original and has not been submitted nor published anywhere else. The findings and results in this work are novel and have not been taken from any other source.

I will be really thankful if you consider this work for possible publication in this reputable Journal.

Best Regards,

Dr Ahmad Albadarin, PhD.

Materials Surface Science Institute,

Department of Chemical and Environmental Sciences,

University of Limerick, Ireland

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RESEARCH HIGHLIGHTS:

- Multi-adsorbent systems containing tea waste (TW) and dolomite (DO) have been tested.
- The effects of contact time, solution pH and adsorption isotherms were investigated.
- Adsorption capacities for Cu and MB were calculated as 237.7 and 150.4 mg.g⁻¹ for DO and TW:DO respectively.
- Solution pH had little effect on the capacity of the TW:DO system, specifying that the system has good potential for practical use.

Preliminary investigation of mixed adsorbents for the removal of copper and methylene blue from aqueous solutions

Ahmad B. Albadarin^{1,2*}, Jiabin Mo¹, Yoann Glocheux¹, Stephen Allen¹, Gavin Walker^{1,2},
Chirangano Mangwandi^{1*}

¹ *Materials Surface Science Institute, Department of Chemical and Environmental Sciences,
University of Limerick, Ireland*

² *School of Chemistry and Chemical Engineering, Queen's University Belfast, Belfast BT9
5AG, Northern Ireland, UK.*

*Corresponding Author

Dr Chirangano Mangwandi

Dr Ahmad B. Albadarin

Tel: +44 (0) 28 9097 4378

Fax: +44 (0) 28 9097 6524

E-mail: c.mangwandi@qub.ac.uk

E-mail: aalbadarin01@qub.ac.uk

Abstract

With most recent studies being focused on the development of advanced chemical adsorbents, this paper investigates the possibility of using two natural low-cost materials for selective adsorption. Multi-adsorbent systems containing tea waste (TW) and dolomite (DO) have been tested for their effectiveness in the removal of copper and methylene blue from aqueous solutions. The effects of contact time, solution pH and adsorption isotherms on the sorption behaviour were investigated. The Langmuir and Freundlich isotherms adequately described the adsorption of copper ions and methylene blue by both materials in different systems. The highest adsorption capacities for Cu and MB were calculated as 237.7 mg/g at pH 4.5 and 150.4 mg/g at pH 7 for DO and TW:DO respectively. Tea waste and dolomite were characterized by Fourier transform infrared spectroscopy, scanning electron microscopy and Energy dispersive X-ray analysis. The removal of Cu and MB by dolomite was mainly via surface complexation while physisorption was responsible for most of the Cu and MB adsorption onto tea waste. Identifying the fundamental mechanisms and behaviour is key to the development of practical multi-adsorbent packed columns.

Keywords: Multi-adsorbents; Wastewater; Adsorption technique; Heavy metals; Dyes

1. Introduction

Dyes (very frequently methylene blue and methyl orange) and heavy metals (copper, cadmium and nickel mostly from the organo-metallic dyes) are dangerous pollutants found in large quantities in wastewaters from textile and paper industries. It is known that heavy metals are toxic and non-biodegradable [1, 2]. Heavy metals have many environmental issues such as animal and plant death, reduced rates of reproduction and the decrease of ecosystem diversity [3]. While dyes are difficult to treat as the colour tends to hold strong even after the conventional removal processes [4]. There are more than 100,000 commercially available dyes with over 700,000 tons produced annually [5]. The presence of some of these dyes even in very small amounts i.e. $< 1 \text{ mg.dm}^{-3}$ is undesirable [6, 7]. Dyes-Heavy metal loaded wastewaters are highly coloured, have a fluctuating pH and regularly contain large amounts of suspended oils. Dyes and heavy metals find their way into the environment, primarily dissolved or suspended in water everyday [8] and create serious damage to the environment by changing the biological life balance in rivers and lakes [9, 10]. Adsorption is a well-established and powerful practice for the removal of dyes and heavy metal pollutants from wastewaters. For these reasons, thousands of investigations have used uncountable adsorbents to remove heavy metals [11] or dyes [12]. Most of these studies focus on single-component aqueous solutions and recently, more research papers have been published dealing with the adsorption of dyes and metals in multi-component aqueous systems [6]. Also, composite adsorbents have been established to adsorb dyes and heavy metals from wastewater such as chitosan/montmorillonite composites [13-15] and fly ash/activated carbon [16]. In previous studies, composite materials were used to selectively adsorb a particular pollutant. Ho and co-workers proved that amino functionalized silica solids can selectively adsorb dye anthraquinone blue in the presence of methylene blue, while, from the same dye mixture, carboxy-functionalized materials adsorb methylene blue

selectively [17]. Prediction of multicomponent adsorption is still one of the most challenging problems in the adsorption field [18]. There is little data available to provide more understanding about the interactions between adsorbents and developing design models for such practical systems is very important [19]. This is the case for many composite materials as well as adsorption processes with multi-adsorbate and multi-adsorbent systems. Dolomite, with a structure of alternative layers of calcite and magnesite, is a potential inexpensive and readily available adsorbent [20]. Many studies showed that dolomite and charred dolomite have the potential to act as adsorbents for reactive dyes and heavy metals [21]. Tea, processed leaves from *Camellia sinensis* species, is the second most common drink being consumed after water with an average daily drinking of 20 billion cups. The producers of making tea drinks face a problem in disposing of the spent tea leaves after the extraction [22, 23]. The feasibility of using the richly available solid waste, spent tea leaves, for the removal of heavy metals and dyes has also been extensively investigated [24]. A good understanding of the effect of adsorbent-adsorbent interactions on selective adsorption is essential as a foundation for selecting the best adsorbent and employing it in an optimal way. Hence, the aim of this research is to clarify the chemical and physical interferences between the two materials, namely tea waste and dolomite, when used for the removal of copper and methylene blue from aqueous solutions. In this paper, the term adsorption will refer to biosorption onto tea waste (TW) and adsorption onto dolomite (DO). Copper ions and methylene blue dye adsorption onto tea waste and dolomite using different factors, such as reaction contact time and pH of solution as well as initial metal and dye concentration on selective adsorption was examined. Recognizing the fundamental mechanisms and behaviour would be useful for practical multi-adsorbent packed columns.

2. Materials and Methods

2.1. Adsorbents and adsorbents

The two low cost materials used in this experiment were tea waste (TW) biosorbent and dolomite (DO) adsorbent. Fine Dolomite ($d_p < 50\mu\text{m}$) was supplied by Killwaughter Chemical Company, UK. The typical chemical composition of the dolomite in the deposit was 44% MgCO_3 and 53% CaCO_3 (obtained by XRD analysis) [25]. The tea waste biosorbent was collected from Queen's University cafeteria; it was washed several times with hot water and dried in a conventional oven at 110°C . The two adsorbents were comprehensively characterized in previous investigations [26, 27]. Copper(II) and Methylene Blue (MB) stock solutions were prepared by dissolving known amounts of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and MB in deionised water. The stock solutions were then diluted to get various initial concentrations. All chemicals were purchased from Sigma Aldrich UK.

2.2. Adsorption Experiment

To investigate the influence of pH on Cu(II) and MB adsorption onto TW and DO, six sets of experiments were prepared: Cu(II) or MB with TW biosorbent; Cu(II) or MB with DO adsorbent and Cu(II) or MB with a mixture of 1:1 TW:DO (w/w%). Samples of 25 cm^3 of adsorbate solutions with $C_o = 120$ and 100 mg/dm^3 of Cu and MB, respectively, were adjusted to different pH values: 2–11. The same procedures were performed to study the effect of contact time and adsorption isotherms. The initial concentrations of Cu(II) for the contact time studies was 200 mg/dm^3 and for MB it was 120 mg/dm^3 . For the adsorption isotherm studies, a concentration of: $C_o = 10\text{--}100\text{ mg/dm}^3$ for Cu(II) and $C_o = 10\text{--}75\text{ mg/dm}^3$ for MB were used. An adsorbent dose of 1 g/dm^3 was used for all experiments at room temperature ($\sim 20^\circ\text{C}$) and a contact time of 4 days to ensure reaching the equilibrium. There were no pH adjustments for contact time and isotherm experiments, so the experimental processes are more environmental friendly. The concentrations of Cu(II) and MB were

analysed using an ICP– OES Thermo Scientific IRIS and UV/Vis spectrophotometer (Perkin Elmer LAMBDA 25, UK), respectively. The amount of Cu(II) and MB adsorbed per unit mass of adsorbent q in (mg/g) and removal percentage were calculated using Eq. (1) and Eq. (2):

$$\text{The percentage removal} = \left[1 - \frac{C_e}{C_o} \right] \times 100\% \quad (1)$$

$$q = \left[\frac{C_o - C_e}{M} \right] \times V \quad (2)$$

Where C_o and C_e (mg/L) are the concentration of adsorbate at initial and equilibrium, respectively, M is the mass of adsorbent (g) and V is the volume (dm³).

2.3. Infrared and SEM measurement

The FT-IR analyses for TW and DO surfaces before and after Cu(II) and MB adsorption were carried out on a Perkin Elmer Spectrum 100 within the range of 400–4000 cm⁻¹. For the SEM analysis and Energy dispersive X-ray (EDX) analysis, TW and DO samples were coated with carbon and vacuumed (5–10 min) for electron reflection prior to analysis on a JEOL-JSM 6400 scanning microscope.

3. Results and Discussion

3.1. Effect of contact time

Figures S1 (a) and (b) are the plots of Cu(II) and MB removal against time for TW and DO materials, respectively. It can be seen that Cu(II) and MB were almost completely removed by dolomite and tea waste after 6 hrs at room temperature (20 °C). The adsorption of Cu(II) and MB dye was fast in the initial stage due to the large number of available binding sites, resulting in a concentration gradient [28]. The removal rate gradually declined with time until equilibrium was achieved. The maximum removal efficiencies of copper ions and MB onto TW and DO were approx. 90% at pH of 5–7. The adsorption capacities of Cu(II) and MB were reduced when the two materials were mixed together; this reduction was more significant in the case of Cu(II). The adsorption capacity of the mixed adsorbent (TW:DO) was reduced to approx. 45% and 85% for Cu and MB, respectively. This reduction is attributed to the change in the sorbent and solution properties such as pH_{PZC} and $pH_{equilibrium}$ [29]. However, results indicate that these pollutants can still be efficiently removed with high selectivity onto the mixed adsorbents.

3.2. Kinetics Modelling

The adsorption mechanism can be investigated using various adsorption kinetics models. The pseudo first- [30] and pseudo second-order [31] models (Eq. 3 and Eq. 4) have been employed to examine the experimental data for the adsorption of Cu(II) and MB by nonlinear regression. The pseudo first-order model equation is given as follow:

$$q_t = q_e (1 - e^{-k_1 t}) \quad (3)$$

The pseudo second-order equation is given as;

$$q_t = \frac{k_2 q_e^2}{(1 + k_2 q_e t)} t \quad (4)$$

The second-order rate constants were used to calculate the initial sorption rate given by:

$$h = k_2 q_e^2 \quad (5)$$

where k_1 (1/min) and k_2 (g/mg min) are the rate constants for first order and second-order models.

The plots of q_t versus t and values of the constants of kinetic models obtained from the plots are given in Figure 1 and Table 1. From Table 1, the pseudo first- and pseudo second-order models fit the kinetic data with adequate accuracy ($R^2 > 0.897$). However, the experimental data demonstrated more agreement with the pseudo second-order model in terms of closer $q_{e,cal}$ values to $q_{e,exp}$ and higher correlation coefficients than the pseudo first-order model. This indicates that the chemical adsorption was the main control process for the TW and DO materials and the uptake capacity is proportional to the number of active sites [32]. Similar trends were reported for the removal of copper onto chitosan-coated sludge [33] and methylene blue onto magnetic graphene-carbon nanotube composite and polyaniline nanotubes base/silica [34, 35]. The rate constants (k_1 and k_2) for both Cu(II) and MB sorption onto the TW biosorbent are higher than that for the DO adsorbent. This indicates that it is faster for Cu(II) and MB–TW systems to reach a specific fractional uptake. Initial adsorption rate (h) values for Cu(II) and MB sorption followed the same trends (Cu(II) (89.07– 110.9 mg/g min) and MB (17.56– 56.65 mg/g min). Also, the Elovich equation was used to evaluate the kinetic sorption data. The linear form of the Elovich equation is given in Eq. 6 below:

$$q_t = 1/\beta \ln(\alpha\beta) + 1/\beta \ln(t) \quad (6)$$

where α is the initial adsorption rate (mg/g min), whilst β is the extent of surface coverage (g/mg) and activation energy of the process.

As can be seen in Table 1, the initial sorption rate (α) is lower in the case of sorption onto the DO system, similar to that of rate constants and initial sorption rate (h) in the pseudo second-

order model. The Elovich equation did not fit the experimental data very well with the regression coefficient, R^2 , within 0.659–0.877, suggesting that sorption systems of this study are maybe homogeneous.

3.3. Effect of solution pH

The pH parameter is associated with the adsorption mechanisms onto the adsorbent/biomass surfaces from water and determines the magnitude of the electrostatic charges [36]. From Figure 2, it can be observed that the uptake of Cu(II) onto the DO is significantly increased from 39% of removal at pH 2 to a maximum removal of 89% at pH 4.5. At this pH value, the main species of copper are Cu(II) free ions which are primarily involved in the removal process. With a pH value greater than 6, immediate precipitation of copper hydroxide takes place especially for high concentration of Cu(II) ions hindering the adsorption or biosorption processes [37]. The adsorption capacity of Cu(II) onto TW was notably lower at pH 4.5 with a maximum percentage removal of 39% at pH 5.5. The relatively lower Cu(II) removal onto TW can be attributed to the surface chemistry properties of TW such as; the surface point of zero charge. The PZC was previously determined to be $\text{pH} = 4$ [27] and had an important effect on the equilibrium ($\text{pH}_{\text{equilibrium}}$). For example, the Cu(II) solution with a $\text{pH}_0 = 5.5$ decreased to $\text{pH}_{\text{eq}} = 4.2$ after being put in contact with TW for 4 days. Similar trends were observed for the biosorption of Cd(II) onto sawdust [1]. Also, it was found that the equilibrium pH for MB solution at $\text{pH}_0 = 10$ was reduce to $\text{pH}_{\text{eq}} = 8.8$ when using the TW:DO mixed adsorbent. However, MB was efficiently removed by TW over the pH range studied, which is attributable to the electrostatic attraction between the negatively charged TW surface and the cationic MB dye molecules [38]. These results demonstrated that pH had little effect on the capacity of the TW:DO system, indicating that the system has good potential for practical use.

3.4. Equilibrium modelling

3.4.1. Langmuir Isotherm

The Langmuir isotherm assumes that the surface of the adsorbent is homogeneous, the adsorption energy is constant over all sites and each site can accommodate only one molecule or atom [39]. The Langmuir adsorption isotherm is given as [40]:

$$q_e = \frac{q_{\max} b C_e}{1 + b C_e} \quad (7)$$

where q_{\max} (mg/g) and b (dm³/mg) are Langmuir constants associated with the capacity and energy of adsorption.

The fundamental characteristics of the Langmuir isotherm can be expressed by a dimensionless separation factor, R_L , defined by:

$$R_L = \frac{1}{1 + (q_{\max} \times b) C_o} \quad (8)$$

The R_L parameter indicates the shape of the isotherm as follows: $R_L > 1$, unfavourable; $R_L = 1$, linear; $0 < R_L < 1$, favourable; $R_L = 0$, irreversible.

3.4.2. Freundlich Isotherm

The Freundlich isotherm explains a particular phenomenon when the adsorption takes place on a heterogeneous surface [41]. The Freundlich isotherm model is given in Eq. 9:

$$q_e = K_F C_e^n \quad (9)$$

where K_F and n are the Freundlich constants.

The Langmuir and Freundlich isotherm constants obtained from non-linear regression fitting are revealed in Table 2. The Langmuir and Freundlich isotherms were able to represent adsorption of copper ions and methylene blue by both materials in different systems (Figure 3 & 4). The adsorption capacity of DO for Cu is significantly higher than TW and the trend is

reversed for MB. It can also be observed that the combination of TW and DO adsorbents will reduce the adsorption capacity towards Cu, while increasing the MB adsorption capacity (Table 2). In general, the sorption capacities were higher for MB than Cu, which may be due to the isotherm experiment being carried out without any pH adjustment. The dimensionless separation factor (R_L) values were close to zero in all cases. This indicates that the adsorption processes of Cu and MB were favourable at the investigated conditions. The R_L values approached zero when TW:DO systems were used demonstrating that the uptake of the Cu and MB in these systems was more favourable. The Freundlich constant, n values in the range of 1.061–3.764 confirmed the process is classified as favourable adsorption [42]. The closer $1/n$ is to zero, the greater the heterogeneity of the adsorbent [43].

3.5. Surface Characteristics of TW and Dolomite

3.5.1. SEM and EDX

The SEM images of the TW and DO samples before and after adsorption of Cu and MB are shown in (Figure 5); experimental conditions: C_o : MB = 120 at pH 7 and Cu = 200 at pH 4.4 and 6 hrs contact time). From Figure 5 (b) and (c), it can be noticed the formation of crystals at the surface of the DO sample after adsorption with Cu and MB. The presence of CuCO_3 is confirmed with the presence of small and abundant crystals on the surface of DO. The development of crystals in the case of the DO– MB sample also suggests the implication of surface precipitation in the case of MB removal by DO. Similar processes were identified by Walker et al. with the removal of Cu^{2+} by half charred dolomite where surface complexation and precipitation were identified as the main removal route (See Figure 6 (a)) [25]. Surface precipitation of dye was reported in other studies and accounted for nearly 70% of dye removal when using lime treatment [44]. For the TW material, very little changes were observed between the samples before and after adsorption of MB and Cu. The absence of obvious surface structure change indicates that no surface precipitation is involved in the

removal of both pollutants by TW. The metal ions and dye molecules may bound to the active sites of the biosorbent through electrostatic attraction or hydrogen bonding (Figure 6 (b)). Heavy metals removal by TW is very often accounted to chemisorption while dyes removal by biosorbents or activated carbon is mainly described through physisorption with minor contribution from chemisorption mechanisms [27, 45]. Table 3 presents the EDX results obtained for the exhausted adsorbents after kinetic experiments. The area analysed was the one presented in Figure 5, focusing on the crystals formed in the case of DO-Cu or DO-MB or on the possibly larger area for the TW-Cu and TW-MB. The thin carbon layer required in the technique shifted all the results obtained for the C content. However, it can be seen that TW samples are carbon rich as expected and DO contains a substantial amount of C, partly accounted for the CO_3^{2-} groups. The EDX method shows that Cu is present in the crystals formed at the surface of DO confirming the surface precipitation phenomenon. The presence of sulphur is probably due to the sulphate groups present in the Cu salt used in the experiment. The EDX technique cannot differentiate between the crystals formed and those in the DO structure. However, due to the experimental conditions, the nature of the copper crystals precipitated are identified as copper hydroxide crystals $\text{Cu}(\text{OH})_2$ with potential existence of sulphate or carbonate groups [46]. The blue macroscopic colour of the DO sample after adsorption of copper confirms this identification. In the case of MB adsorption onto DO, the relatively high amount of sulphur can be accounted to the sulphur atoms present in the MB molecule. As the analysis area is focusing only on the crystals visible in Figure 5 (c), the value of nearly 7% sulphur has to be balanced. Regarding the TW-Cu sample, the presence of 4.3% Cu at the surface of the sample is equivalent to 43 mg/g of Cu adsorption capacity, which is very close to the adsorption capacity calculated in the kinetic experiments (Table 1). The EDX analysis in the present case was carried out over the total surface of the sample from Figure 5 (e) as no surface precipitation was noticed. The very low content of

sulphur on the TW-Cu sample indicates that the sulphate groups from the copper salt are not adsorbed by the biosorbents. The copper sorption onto the TW surface is therefore very selective. The higher content of sulphur on the surface of the TW-MB sample confirms the adsorption of MB. The EDX technique confirmed the precipitation of both Cu and MB onto the surface of DO and suggested that the sorption of these pollutants onto TW was either due to chemisorption or physisorption.

3.5.2. FTIR analysis

Figure 7 illustrates the FTIR analysis of the DO samples before and after adsorption of MB and Cu. The spectrum of the DO sample shows several peaks around 1400 cm^{-1} which are related to the CO_3^{2-} groups and are attributed to the C-O bonds present in the sample [26].

Bands around 2500 cm^{-1} are assigned to water molecules bonded to the sample [36]. The net peaks detected after the adsorption of MB found around 3414 cm^{-1} are attributed to OH^- bonds and thus show the hydration of the DO sample and possible links with MB molecules through chemisorption. The relatively high peak at 3430 cm^{-1} confirms the presence of hydroxyl groups and the formation of $\text{Cu}(\text{OH})_2$ complexes. A sharp peak observable at 714 cm^{-1} after Cu sorption was also noticed by Ippolito et al. and attributed to the presence of CaO [47]. The formation of complexes in the form of $\text{Ca/Cu}-(\text{OH})_x$ is thus highly probable. A partial ion-exchange mechanism between Ca^{2+} and Cu^{2+} in the removal of copper from wastewater was also reported by Walker et al. [25]. The FTIR analysis for the TW sample shown in Figure 8, demonstrated major peaks indicating many functional groups such as $-\text{NH}_2$ and $-\text{OH}$ groups of proteins and glucose; $-\text{CH}$ stretching and $>\text{C}=\text{O}$ ester stretching vibration of triglycerides; this stretching mode conjugated with the NH_2 (amide 1 band) [27].

After MB adsorption onto TW two main peaks can be seen at 1383 and 1337 cm^{-1} and most of the peaks already present are enhanced. The FTIR peaks characteristic of MB molecules overlap with peaks from the TW sample as most chemical groups present in MB are present

in TW. The broad peak visible around 3230– 3270 cm^{-1} is linked to the N-H bonding from MB. The peaks around 1737 and 1160 cm^{-1} account for the sulphate groups and are naturally present on the TW sample [48]. It is thus interesting to note that after Cu adsorption this peak is relatively high, thus indicating a sorption of the sulphate groups from the copper salt as well. Negatively charged ions are necessary to counter-balance the sorption of Cu^{2+} onto TW, also SO_4^{2-} is involved in this process. The sorption of both anions and cations is characteristics of physisorption where both ions co-habit in the diffuse layer [49]. EDX analysis coupled with FTIR investigation showed that surface complexation was the main route of removal for Cu and MB by DO. Using data from the pH study it can be concluded that physisorption was responsible for most of Cu and MB adsorption onto TW even if chemisorption was also contributing to the removal of MB by TW.

3.6. Comparison of adsorption capacity with composite adsorbents

A comparison was carried out between the results of the adsorption capacities of tea waste and dolomite multi-adsorbent system dyes and chemically prepared composite adsorbents towards copper ions and methylene blue (Table 4). Ignoring the different experimental conditions used, it can be seen that the adsorption capacities obtained in this study are comparable with those reported by other researchers. This indicates that tea waste and dolomite multi-adsorbents can be classified as one of the effective adsorption systems for this purpose. The two substances in this investigation were physically mixed without any chemical modifications. Once more, this implies that environmentally friendly composite adsorbents can be produced at low cost and very little effort without any chemical alterations.

4. Conclusion

The selectivity of tea waste and dolomite for copper and methylene blue and the influence of contact time, solution pH and initial pollutant concentration on adsorption capacities was examined. The adsorption kinetics could be explained by the pseudo-second-order model. The maximum removal capacity of Cu onto both adsorbents was achieved at pH = 4.5, while MB was optimally removed over the pH range studied with removal percentages of over 90%. The present investigation indicated that tea waste and dolomite can concurrently be effectively used to remove copper and methylene blue from aqueous solution. Further studies are required to examine the effect of the chemistry of solution and the design and scale-up of fixed-bed adsorption columns.

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1 **Preliminary investigation of mixed adsorbents for the removal of copper and methylene**
2 **blue from aqueous solutions**

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5 Ahmad B. Albadarin^{1,2*}, Jiabin Mo¹, Yoann Glocheux¹, Stephen Allen¹, Gavin Walker^{1,2},
6 Chirangano Mangwandi^{1*}

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8
9 ¹ *Materials Surface Science Institute, Department of Chemical and Environmental Sciences,*
10 *University of Limerick, Ireland*

11 ² *School of Chemistry and Chemical Engineering, Queen’s University Belfast, Belfast BT9*
12 *5AG, Northern Ireland, UK.*

13
14
15 *Corresponding Author
16 Dr Chirangano Mangwandi
17 Dr Ahmad B. Albadarin
18 Tel: +44 (0) 28 9097 4378
19 Fax: +44 (0) 28 9097 6524
20 E-mail: c.mangwandi@qub.ac.uk
21 E-mail: aalbadarin01@qub.ac.uk
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26 **Abstract**

27 With most recent studies being focused on the development of advanced chemical
28 adsorbents, this paper investigates the possibility of using two natural low-cost materials for
29 selective adsorption. Multi-adsorbent systems containing tea waste (TW) and dolomite (DO)
30 have been tested for their effectiveness in the removal of copper and methylene blue from
31 aqueous solutions. The effects of contact time, solution pH and adsorption isotherms on the
32 sorption behaviour were investigated. The Langmuir and Freundlich isotherms adequately
33 described the adsorption of copper ions and methylene blue by both materials in different
34 systems. The highest adsorption capacities for Cu and MB were calculated as 237.7 mg/g at
35 pH 4.5 and 150.4 mg/g at pH 7 for DO and TW:DO respectively. Tea waste and dolomite
36 were characterized by Fourier transform infrared spectroscopy, scanning electron microscopy
37 and Energy dispersive X-ray analysis. The removal of Cu and MB by dolomite was mainly
38 via surface complexation while physisorption was responsible for most of the Cu and MB
39 adsorption onto tea waste. Identifying the fundamental mechanisms and behaviour is key to
40 the development of practical multi-adsorbent packed columns.

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42 **Keywords:** Multi-adsorbents; Wastewater; Adsorption technique; Heavy metals; Dyes

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1. Introduction

Dyes (very frequently methylene blue and methyl orange) and heavy metals (copper, cadmium and nickel mostly from the organo-metallic dyes) are dangerous pollutants found in large quantities in wastewaters from textile and paper industries. It is known that heavy metals are toxic and non-biodegradable [1, 2]. Heavy metals have many environmental issues such as animal and plant death, reduced rates of reproduction and the decrease of ecosystem diversity [3]. While dyes are difficult to treat as the colour tends to hold strong even after the conventional removal processes [4]. There are more than 100,000 commercially available dyes with over 700,000 tons produced annually [5]. The presence of some of these dyes even in very small amounts i.e. $< 1 \text{ mg.dm}^{-3}$ is undesirable [6, 7]. Dyes-Heavy metal loaded wastewaters are highly coloured, have a fluctuating pH and regularly contain large amounts of suspended oils. Dyes and heavy metals find their way into the environment, primarily dissolved or suspended in water everyday [8] and create serious damage to the environment by changing the biological life balance in rivers and lakes [9, 10]. Adsorption is a well-established and powerful practice for the removal of dyes and heavy metal pollutants from wastewaters. For these reasons, thousands of investigations have used uncountable adsorbents to remove heavy metals [11] or dyes [12]. Most of these studies focus on single-component aqueous solutions and recently, more research papers have been published dealing with the adsorption of dyes and metals in multi-component aqueous systems [6]. Also, composite adsorbents have been established to adsorb dyes and heavy metals from wastewater such as chitosan/montmorillonite composites [13-15] and fly ash/activated carbon [16]. In previous studies, composite materials were used to selectively adsorb a particular pollutant. Ho and co-workers proved that amino functionalized silica solids can selectively adsorb dye anthraquinone blue in the presence of methylene blue, while, from the same dye mixture, carboxy-functionalized materials adsorb methylene blue

selectively [17]. Prediction of multicomponent adsorption is still one of the most challenging problems in the adsorption field [18]. There is little data available to provide more understanding about the interactions between adsorbents and developing design models for such practical systems is very important [19]. This is the case for many composite materials as well as adsorption processes with multi-adsorbate and multi-adsorbent systems. Dolomite, with a structure of alternative layers of calcite and magnesite, is a potential inexpensive and readily available adsorbent [20]. Many studies showed that dolomite and charred dolomite have the potential to act as adsorbents for reactive dyes and heavy metals [21]. Tea, processed leaves from *Camellia sinensis* species, is the second most common drink being consumed after water with an average daily drinking of 20 billion cups. The producers of making tea drinks face a problem in disposing of the spent tea leaves after the extraction [22, 23]. The feasibility of using the richly available solid waste, spent tea leaves, for the removal of heavy metals and dyes has also been extensively investigated [24]. A good understanding of the effect of adsorbent-adsorbent interactions on selective adsorption is essential as a foundation for selecting the best adsorbent and employing it in an optimal way. Hence, the aim of this research is to clarify the chemical and physical interferences between the two materials, namely tea waste and dolomite, when used for the removal of copper and methylene blue from aqueous solutions. In this paper, the term adsorption will refer to biosorption onto tea waste (TW) and adsorption onto dolomite (DO). Copper ions and methylene blue dye adsorption onto tea waste and dolomite using different factors, such as reaction contact time and pH of solution as well as initial metal and dye concentration on selective adsorption was examined. Recognizing the fundamental mechanisms and behaviour would be useful for practical multi-adsorbent packed columns.

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2. Materials and Methods

2.1. Adsorbents and adsorbates

The two low cost materials used in this experiment were tea waste (TW) biosorbent and dolomite (DO) adsorbent. Fine Dolomite ($d_p < 50\mu\text{m}$) was supplied by Killwaughter Chemical Company, UK. The typical chemical composition of the dolomite in the deposit was 44% MgCO_3 and 53% CaCO_3 (obtained by XRD analysis) [25]. The tea waste biosorbent was collected from Queen's University cafeteria; it was washed several times with hot water and dried in a conventional oven at 110°C . The two adsorbents were comprehensively characterized in previous investigations [26, 27]. Copper(II) and Methylene Blue (MB) stock solutions were prepared by dissolving known amounts of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and MB in deionised water. The stock solutions were then diluted to get various initial concentrations. All chemicals were purchased from Sigma Aldrich UK.

2.2. Adsorption Experiment

To investigate the influence of pH on Cu(II) and MB adsorption onto TW and DO, six sets of experiments were prepared: Cu(II) or MB with TW biosorbent; Cu(II) or MB with DO adsorbent and Cu(II) or MB with a mixture of 1:1 TW:DO (w/w%). Samples of 25 cm^3 of adsorbate solutions with $C_o = 120$ and 100 mg/dm^3 of Cu and MB, respectively, were adjusted to different pH values: 2–11. The same procedures were performed to study the effect of contact time and adsorption isotherms. The initial concentrations of Cu(II) for the contact time studies was 200 mg/dm^3 and for MB it was 120 mg/dm^3 . For the adsorption isotherm studies, a concentration of: $C_o = 10\text{--}100\text{ mg/dm}^3$ for Cu(II) and $C_o = 10\text{--}75\text{ mg/dm}^3$ for MB were used. An adsorbent dose of 1 g/dm^3 was used for all experiments at room temperature ($\sim 20^\circ\text{C}$) and a contact time of 4 days to ensure reaching the equilibrium. There were no pH adjustments for contact time and isotherm experiments, so the experimental processes are more environmental friendly. The concentrations of Cu(II) and MB were

126 analysed using an ICP-OES Thermo Scientific IRIS and UV/Vis spectrophotometer (Perkin
 127 Elmer LAMBDA 25, UK), respectively. The amount of Cu(II) and MB adsorbed per unit
 128 mass of adsorbent q in (mg/g) and removal percentage were calculated using Eq. (1) and Eq.
 129 (2):

$$130 \quad \text{The percentage removal} = \left[1 - \frac{C_e}{C_o} \right] \times 100\% \quad (1)$$

$$131 \quad q = \left[\frac{C_o - C_e}{M} \right] \times V \quad (2)$$

132 Where C_o and C_e (mg/L) are the concentration of adsorbate at initial and equilibrium,
 133 respectively, M is the mass of adsorbent (g) and V is the volume (dm³).

134 **2.3. Infrared and SEM measurement**

135 The FT-IR analyses for TW and DO surfaces before and after Cu(II) and MB adsorption were
 136 carried out on a Perkin Elmer Spectrum 100 within the range of 400–4000 cm⁻¹. For the
 137 SEM analysis and Energy dispersive X-ray (EDX) analysis, TW and DO samples were
 138 coated with carbon and vacuumed (5–10 min) for electron reflection prior to analysis on a
 139 JEOL-JSM 6400 scanning microscope.

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3. Results and Discussion

3.1. Effect of contact time

Figures S1 (a) and (b) are the plots of Cu(II) and MB removal against time for TW and DO materials, respectively. It can be seen that Cu(II) and MB were almost completely removed by dolomite and tea waste after 6 hrs at room temperature (20 °C). The adsorption of Cu(II) and MB dye was fast in the initial stage due to the large number of available binding sites, resulting in a concentration gradient [28]. The removal rate gradually declined with time until equilibrium was achieved. The maximum removal efficiencies of copper ions and MB onto TW and DO were approx. 90% at pH of 5–7. The adsorption capacities of Cu(II) and MB were reduced when the two materials were mixed together; this reduction was more significant in the case of Cu(II). The adsorption capacity of the mixed adsorbent (TW:DO) was reduced to approx. 45% and 85% for Cu and MB, respectively. This reduction is attributed to the change in the sorbent and solution properties such as pH_{PZC} and $pH_{equilibrium}$ [29]. However, results indicate that these pollutants can still be efficiently removed with high selectivity onto the mixed adsorbents.

3.2. Kinetics Modelling

The adsorption mechanism can be investigated using various adsorption kinetics models. The pseudo first- [30] and pseudo second-order [31] models (Eq. 3 and Eq. 4) have been employed to examine the experimental data for the adsorption of Cu(II) and MB by nonlinear regression. The pseudo first-order model equation is given as follow:

$$q_t = q_e (1 - e^{-k_1 t}) \quad (3)$$

The pseudo second-order equation is given as;

$$q_t = \frac{k_2 q_e^2}{(1 + k_2 q_e t)} t \quad (4)$$

The second-order rate constants were used to calculate the initial sorption rate given by:

$$h = k_2 q_e^2 \quad (5)$$

where k_1 (1/min) and k_2 (g/mg min) are the rate constants for first order and second-order models.

The plots of q_t versus t and values of the constants of kinetic models obtained from the plots are given in Figure 1 and Table 1. From Table 1, the pseudo first- and pseudo second-order models fit the kinetic data with adequate accuracy ($R^2 > 0.897$). However, the experimental data demonstrated more agreement with the pseudo second-order model in terms of closer $q_{e,cal}$ values to $q_{e,exp}$ and higher correlation coefficients than the pseudo first-order model. This indicates that the chemical adsorption was the main control process for the TW and DO materials and the uptake capacity is proportional to the number of active sites [32]. Similar trends were reported for the removal of copper onto chitosan-coated sludge [33] and methylene blue onto magnetic graphene-carbon nanotube composite and polyaniline nanotubes base/silica [34, 35]. The rate constants (k_1 and k_2) for both Cu(II) and MB sorption onto the TW biosorbent are higher than that for the DO adsorbent. This indicates that it is faster for Cu(II) and MB-TW systems to reach a specific fractional uptake. Initial adsorption rate (h) values for Cu(II) and MB sorption followed the same trends (Cu(II) (89.07–110.9 mg/g min) and MB (17.56–56.65 mg/g min). Also, the Elovich equation was used to evaluate the kinetic sorption data. The linear form of the Elovich equation is given in Eq. 6 below:

$$q_t = 1/\beta \ln(\alpha\beta) + 1/\beta \ln(t) \quad (6)$$

where α is the initial adsorption rate (mg/g min), whilst β is the extent of surface coverage (g/mg) and activation energy of the process.

As can be seen in Table 1, the initial sorption rate (α) is lower in the case of sorption onto the DO system, similar to that of rate constants and initial sorption rate (h) in the pseudo second-

order model. The Elovich equation did not fit the experimental data very well with the regression coefficient, R^2 , within 0.659–0.877, suggesting that sorption systems of this study are maybe homogeneous.

3.3. Effect of solution pH

The pH parameter is associated with the adsorption mechanisms onto the adsorbent/biomass surfaces from water and determines the magnitude of the electrostatic charges [36]. From Figure 2, it can be observed that the uptake of Cu(II) onto the DO is significantly increased from 39% of removal at pH 2 to a maximum removal of 89% at pH 4.5. At this pH value, the main species of copper are Cu(II) free ions which are primarily involved in the removal process. With a pH value greater than 6, immediate precipitation of copper hydroxide takes place especially for high concentration of Cu(II) ions hindering the adsorption or biosorption processes [37]. The adsorption capacity of Cu(II) onto TW was notably lower at pH 4.5 with a maximum percentage removal of 39% at pH 5.5. The relatively lower Cu(II) removal onto TW can be attributed to the surface chemistry properties of TW such as; the surface point of zero charge. The PZC was previously determined to be $\text{pH} = 4$ [27] and had an important effect on the equilibrium ($\text{pH}_{\text{equilibrium}}$). For example, the Cu(II) solution with a $\text{pH}_0 = 5.5$ decreased to $\text{pH}_{\text{eq}} = 4.2$ after being put in contact with TW for 4 days. Similar trends were observed for the biosorption of Cd(II) onto sawdust [1]. Also, it was found that the equilibrium pH for MB solution at $\text{pH}_0 = 10$ was reduce to $\text{pH}_{\text{eq}} = 8.8$ when using the TW:DO mixed adsorbent. However, MB was efficiently removed by TW over the pH range studied, which is attributable to the electrostatic attraction between the negatively charged TW surface and the cationic MB dye molecules [38]. These results demonstrated that pH had little effect on the capacity of the TW:DO system, indicating that the system has good potential for practical use.

219 3.4. Equilibrium modelling

220 3.4.1. Langmuir Isotherm

221 The Langmuir isotherm assumes that the surface of the adsorbent is homogeneous, the
222 adsorption energy is constant over all sites and each site can accommodate only one molecule
223 or atom [39]. The Langmuir adsorption isotherm is given as [40]:

$$224 \quad q_e = \frac{q_{\max} b C_e}{1 + b C_e} \quad (7)$$

225 where q_{\max} (mg/g) and b (dm³/mg) are Langmuir constants associated with the capacity and
226 energy of adsorption.

227 The fundamental characteristics of the Langmuir isotherm can be expressed by a
228 dimensionless separation factor, R_L , defined by:

$$229 \quad R_L = \frac{1}{1 + (q_{\max} \times b) C_o} \quad (8)$$

230 The R_L parameter indicates the shape of the isotherm as follows: $R_L > 1$, unfavourable; $R_L = 1$,
231 linear; $0 < R_L < 1$, favourable; $R_L = 0$, irreversible.

232 3.4.2. Freundlich Isotherm

233 The Freundlich isotherm explains a particular phenomenon when the adsorption takes place
234 on a heterogeneous surface [41]. The Freundlich isotherm model is given in Eq. 9:

$$235 \quad q_e = K_F C_e^n \quad (9)$$

236 where K_F and n are the Freundlich constants.

237 The Langmuir and Freundlich isotherm constants obtained from non-linear regression fitting
238 are revealed in Table 2. The Langmuir and Freundlich isotherms were able to represent
239 adsorption of copper ions and methylene blue by both materials in different systems (Figure 3
240 & 4). The adsorption capacity of DO for Cu is significantly higher than TW and the trend is

reversed for MB. It can also be observed that the combination of TW and DO adsorbents will reduce the adsorption capacity towards Cu, while increasing the MB adsorption capacity (Table 2). In general, the sorption capacities were higher for MB than Cu, which may be due to the isotherm experiment being carried out without any pH adjustment. The dimensionless separation factor (R_L) values were close to zero in all cases. This indicates that the adsorption processes of Cu and MB were favourable at the investigated conditions. The R_L values approached zero when TW:DO systems were used demonstrating that the uptake of the Cu and MB in these systems was more favourable. The Freundlich constant, n values in the range of 1.061–3.764 confirmed the process is classified as favourable adsorption [42]. The closer $1/n$ is to zero, the greater the heterogeneity of the adsorbent [43].

3.5. Surface Characteristics of TW and Dolomite

3.5.1. SEM and EDX

The SEM images of the TW and DO samples before and after adsorption of Cu and MB are shown in (Figure 5); experimental conditions: C_0 : MB = 120 at pH 7 and Cu = 200 at pH 4.4 and 6 hrs contact time). From Figure 5 (b) and (c), it can be noticed the formation of crystals at the surface of the DO sample after adsorption with Cu and MB. The presence of CuCO_3 is confirmed with the presence of small and abundant crystals on the surface of DO. The development of crystals in the case of the DO–MB sample also suggests the implication of surface precipitation in the case of MB removal by DO. Similar processes were identified by Walker et al. with the removal of Cu^{2+} by half charred dolomite where surface complexation and precipitation were identified as the main removal route (See Figure 6 (a)) [25]. Surface precipitation of dye was reported in other studies and accounted for nearly 70% of dye removal when using lime treatment [44]. For the TW material, very little changes were observed between the samples before and after adsorption of MB and Cu. The absence of obvious surface structure change indicates that no surface precipitation is involved in the

removal of both pollutants by TW. The metal ions and dye molecules may bound to the active sites of the biosorbent through electrostatic attraction or hydrogen bonding (Figure 6 (b)). Heavy metals removal by TW is very often accounted to chemisorption while dyes removal by biosorbents or activated carbon is mainly described through physisorption with minor contribution from chemisorption mechanisms [27, 45]. Table 3 presents the EDX results obtained for the exhausted adsorbents after kinetic experiments. The area analysed was the one presented in Figure 5, focusing on the crystals formed in the case of DO–Cu or DO–MB or on the possibly larger area for the TW–Cu and TW–MB. The thin carbon layer required in the technique shifted all the results obtained for the C content. However, it can be seen that TW samples are carbon rich as expected and DO contains a substantial amount of C, partly accounted for the CO_3^{2-} groups. The EDX method shows that Cu is present in the crystals formed at the surface of DO confirming the surface precipitation phenomenon. The presence of sulphur is probably due to the sulphate groups present in the Cu salt used in the experiment. The EDX technique cannot differentiate between the crystals formed and those in the DO structure. However, due to the experimental conditions, the nature of the copper crystals precipitated are identified as copper hydroxide crystals $\text{Cu}(\text{OH})_2$ with potential existence of sulphate or carbonate groups [46]. The blue macroscopic colour of the DO sample after adsorption of copper confirms this identification. In the case of MB adsorption onto DO, the relatively high amount of sulphur can be accounted to the sulphur atoms present in the MB molecule. As the analysis area is focusing only on the crystals visible in Figure 5 (c), the value of nearly 7% sulphur has to be balanced. Regarding the TW–Cu sample, the presence of 4.3% Cu at the surface of the sample is equivalent to 43 mg/g of Cu adsorption capacity, which is very close to the adsorption capacity calculated in the kinetic experiments (Table 1). The EDX analysis in the present case was carried out over the total surface of the sample from Figure 5 (e) as no surface precipitation was noticed. The very low content of

291 sulphur on the TW–Cu sample indicates that the sulphate groups from the copper salt are not
292 adsorbed by the biosorbents. The copper sorption onto the TW surface is therefore very
293 selective. The higher content of sulphur on the surface of the TW–MB sample confirms the
294 adsorption of MB. The EDX technique confirmed the precipitation of both Cu and MB onto
295 the surface of DO and suggested that the sorption of these pollutants onto TW was either due
296 to chemisorption or physisorption.

297 3.5.2. FTIR analysis

298 Figure 7 illustrates the FTIR analysis of the DO samples before and after adsorption of MB
299 and Cu. The spectrum of the DO sample shows several peaks around 1400 cm^{-1} which are
300 related to the CO_3^{2-} groups and are attributed to the C–O bonds present in the sample [26].
301 Bands around 2500 cm^{-1} are assigned to water molecules bonded to the sample [36]. The net
302 peaks detected after the adsorption of MB found around 3414 cm^{-1} are attributed to OH^\square
303 bonds and thus show the hydration of the DO sample and possible links with MB molecules
304 through chemisorption. The relatively high peak at 3430 cm^{-1} confirms the presence of
305 hydroxyl groups and the formation of $\text{Cu}(\text{OH})_2$ complexes. A sharp peak observable at 714
306 cm^{-1} after Cu sorption was also noticed by Ippolito et al. and attributed to the presence of
307 CaO [47]. The formation of complexes in the form of $\text{Ca/Cu}-(\text{OH})_x$ is thus highly probable. A
308 partial ion-exchange mechanism between Ca^{2+} and Cu^{2+} in the removal of copper from
309 wastewater was also reported by Walker et al. [25]. The FTIR analysis for the TW sample
310 shown in Figure 8, demonstrated major peaks indicating many functional groups such as
311 $-\text{NH}_2$ and $-\text{OH}$ groups of proteins and glucose; $-\text{CH}$ stretching and $>\text{C}=\text{O}$ ester stretching
312 vibration of triglycerides; this stretching mode conjugated with the NH_2 (amide 1 band) [27].
313 After MB adsorption onto TW two main peaks can be seen at 1383 and 1337 cm^{-1} and most
314 of the peaks already present are enhanced. The FTIR peaks characteristic of MB molecules
315 overlap with peaks from the TW sample as most chemical groups present in MB are present

in TW. The broad peak visible around 3230–3270 cm^{-1} is linked to the N-H bonding from MB. The peaks around 1737 and 1160 cm^{-1} account for the sulphate groups and are naturally present on the TW sample [48]. It is thus interesting to note that after Cu adsorption this peak is relatively high, thus indicating a sorption of the sulphate groups from the copper salt as well. Negatively charged ions are necessary to counter-balance the sorption of Cu^{2+} onto TW, also SO_4^{2-} is involved in this process. The sorption of both anions and cations is characteristics of physisorption where both ions co-habit in the diffuse layer [49]. EDX analysis coupled with FTIR investigation showed that surface complexation was the main route of removal for Cu and MB by DO. Using data from the pH study it can be concluded that physisorption was responsible for most of Cu and MB adsorption onto TW even if chemisorption was also contributing to the removal of MB by TW.

3.6. Comparison of adsorption capacity with composite adsorbents

A comparison was carried out between the results of the adsorption capacities of tea waste and dolomite multi-adsorbent system dyes and chemically prepared composite adsorbents towards copper ions and methylene blue (Table 4). Ignoring the different experimental conditions used, it can be seen that the adsorption capacities obtained in this study are comparable with those reported by other researchers. This indicates that tea waste and dolomite multi-adsorbents can be classified as one of the effective adsorption systems for this purpose. The two substances in this investigation were physically mixed without any chemical modifications. Once more, this implies that environmentally friendly composite adsorbents can be produced at low cost and very little effort without any chemical alterations.

4. Conclusion

The selectivity of tea waste and dolomite for copper and methylene blue and the influence of contact time, solution pH and initial pollutant concentration on adsorption capacities was examined. The adsorption kinetics could be explained by the pseudo-second-order model. The maximum removal capacity of Cu onto both adsorbents was achieved at $\text{pH} = 4.5$, while MB was optimally removed over the pH range studied with removal percentages of over 90%. The present investigation indicated that tea waste and dolomite can concurrently be effectively used to remove copper and methylene blue from aqueous solution. Further studies are required to examine the effect of the chemistry of solution and the design and scale-up of fixed-bed adsorption columns.

366 5. References

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Table 1: Pseudo first-order and pseudo second-order model constants for Cu(II) and MB sorption onto tea waste and dolomite at different systems.

Adsorbent		Pseudo first-order model				Pseudo second-order model			Elovich equation		
		$q_{e,exp}$	$q_{e,cal}$	k_1	R^2	$q_{e,cal}$	k_2	R^2	α	β	R^2
		(mg/g)	(mg/g)	(1/min)		(mg/g)	(g/mg min)				
Cu	TW	60.80	55.68	0.221	0.901	59.26	0.005	0.967	0.532	5.376	0.853
	DO	186.5	177.9	0.011	0.897	193.8	0.001	0.910	0.019	29.12	0.823
	TW + DO	82.09	74.23	0.480	0.908	79.34	0.009	0.947	0.438	5.135	0.837
MB	TW	111.6	109.4	0.407	0.995	112.8	0.007	0.999	0.598	15.12	0.659
	DO	67.75	57.70	0.126	0.896	62.65	0.003	0.963	0.108	10.90	0.877
	TW + DO	107.7	102.6	0.486	0.991	105.3	0.010	0.997	0.689	14.13	0.661

Table 2: The Langmuir and Freundlich isotherm constants for Cu(II) and MB sorption onto tea waste and dolomite at different systems.

Adsorbent		Langmuir isotherm model				Freundlich isotherm model		
		q_{\max}	b	$R_L (\times 10^3)$	R^2	K_F	n	R^2
		(mg/g)	(dm ³ /mg)			(mg/g)(dm ³ /mg) ^{1/n}		
Cu	TW	77.31	0.015	8.549	0.960	2.402	1.492	0.979
	DO	237.7	0.022	1.883	0.990	6.607	1.244	0.983
	TW + DO	38.2	0.239	1.094	0.984	12.69	3.764	0.922
MB	TW	130.5	0.271	0.376	0.946	28.02	1.564	0.912
	DO	113.3	0.018	6.493	0.901	4.256	1.520	0.925
	TW + DO	150.4	0.262	0.338	0.967	30.92	1.445	0.944

Table 3: EDX analysis results expressed in % w/w.

	Elemental composition in % w/w					
	C	O	Mg	S	Ca	Cu
DO-Cu	22.80	29.88	2.77	4.33	14.55	25.66
DO-MB	18.42	43.33	6.64	6.21	25.40	-
TW-Cu	65.41	29.82	-	0.46	-	4.31
TW-MB	71.60	27.00	-	1.40	-	-

Table 4: Comparison of adsorption capacities of the TW:DO system with composite adsorbents in literature.

Adsorbents	Pollutant (Cu or MB)	Adsorption capacity (mg/g)	Max conc. Studied	Best fit isotherm	Ref.
Bentonite–polyacrylamide	Cu(II)	32.8	15 ppm	Langmuir	[2]
Ligand modified composite	Cu(II)	182.1	60 ppm	Langmuir	[14]
Alginate/Mauritanian clay (Na-ZS26)	Cu(II)	15.1	200 ppm	Langmuir	[15]
Tea waste + Dolomite	Cu(II)	38.1	100 ppm	Langmuir	Current study
Alumina-carbon	MB	1152.3	420 ppm	Redlich-Peterson	[10]
Magnetic graphene-carbon nanotube	MB	65.79	35 ppm	Langmuir	[34]
Polyaniline nanotubes base/silica	MB	10.3	10 ppm	Langmuir	[35]
Tea waste + Dolomite	MB	150.4	75 ppm	Langmuir	Current study

Figure

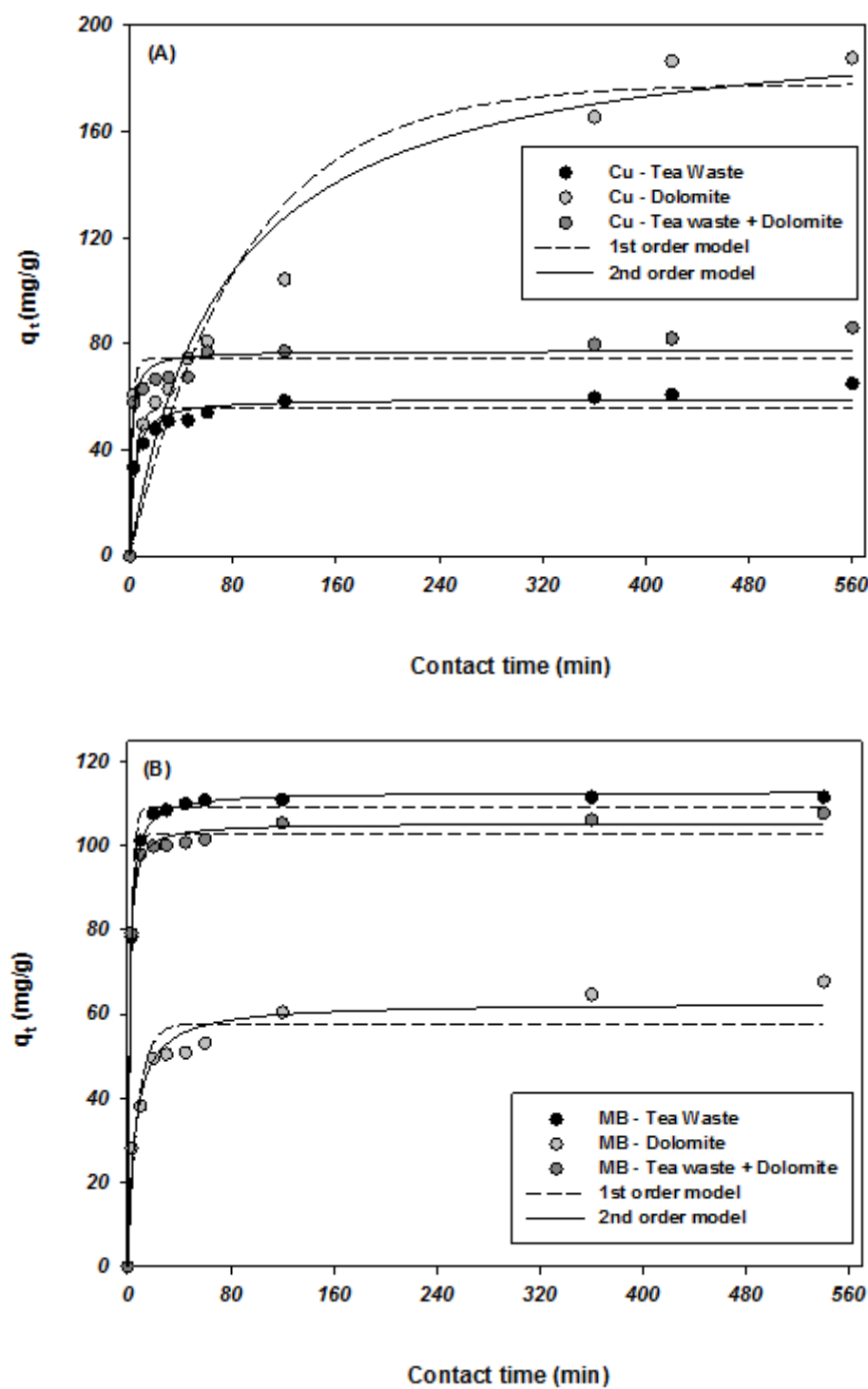


Figure 1: The fitting of pseudo first- and second-order models for Cr(II) and MB removal onto TW and DO.

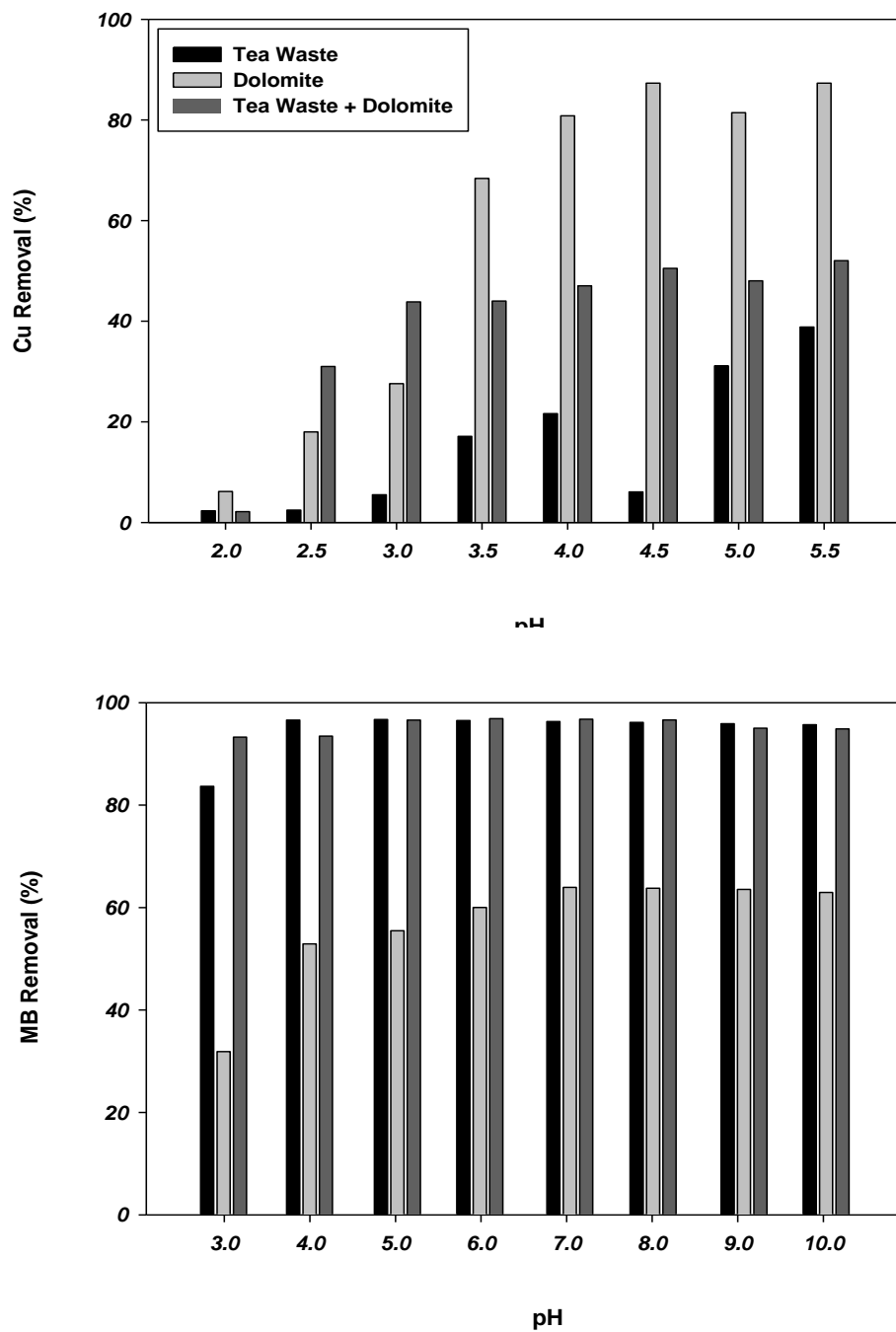


Figure 2: Effect of pH on the removal of Cu(II) and MB onto TW and DO.

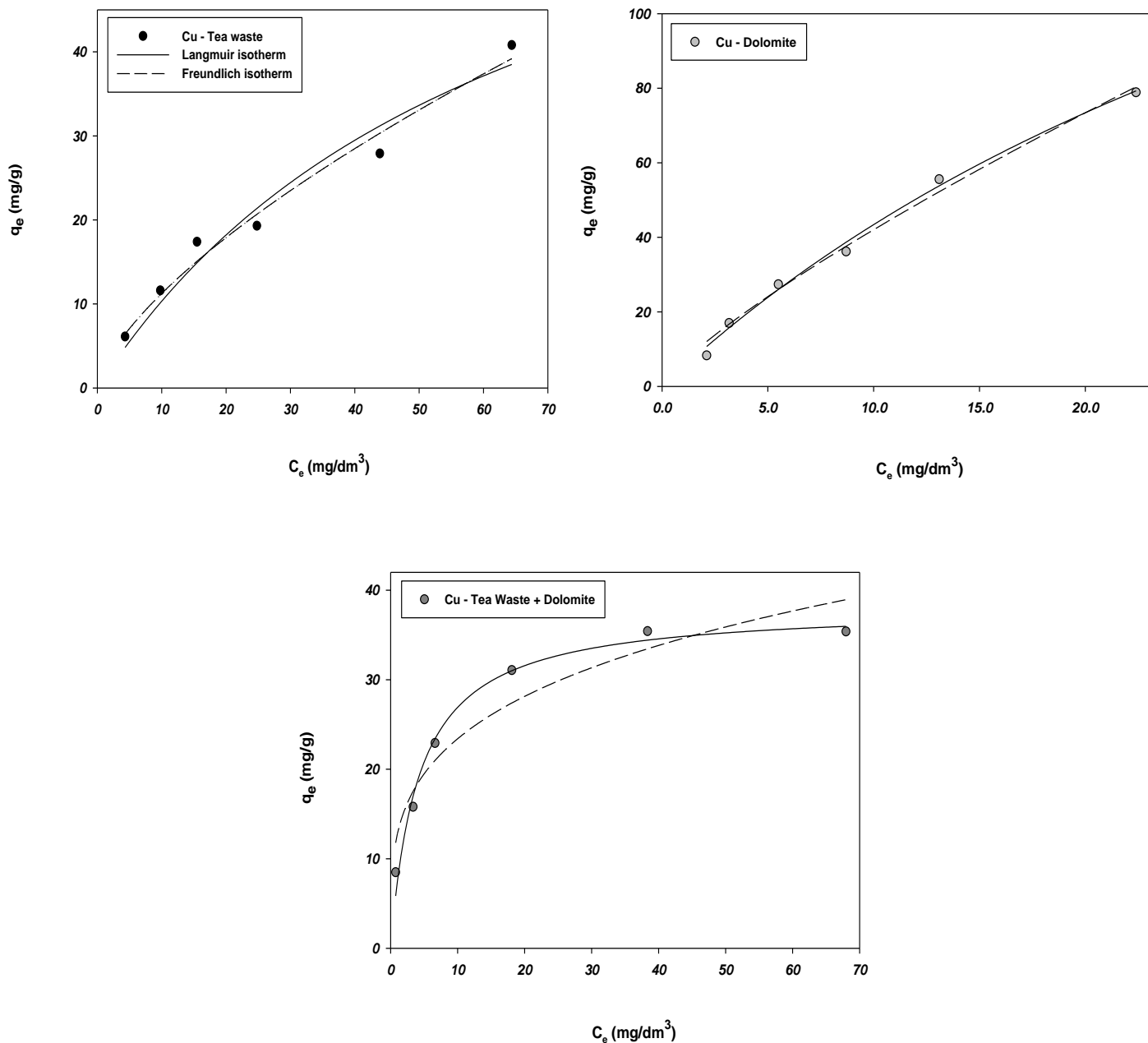


Figure 3: Non-linear forms of Langmuir and Freundlich adsorption isotherm plots of Cu adsorption onto Tea Waste (TW) and Dolomite (DO).

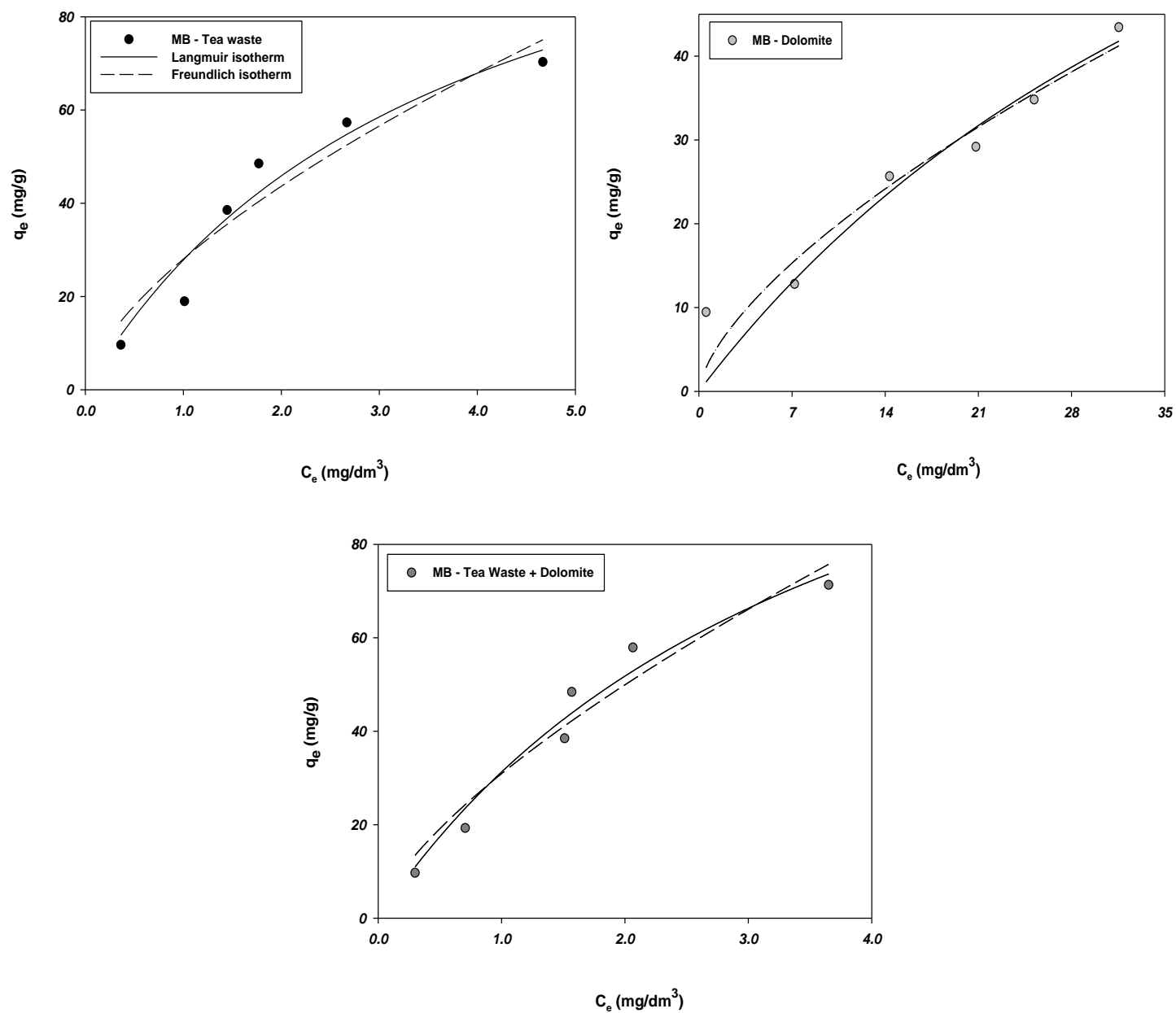


Figure 4: Non-linear forms of Langmuir and Freundlich adsorption isotherm plots of MB onto Tea Waste (TW) and Dolomite (DO).

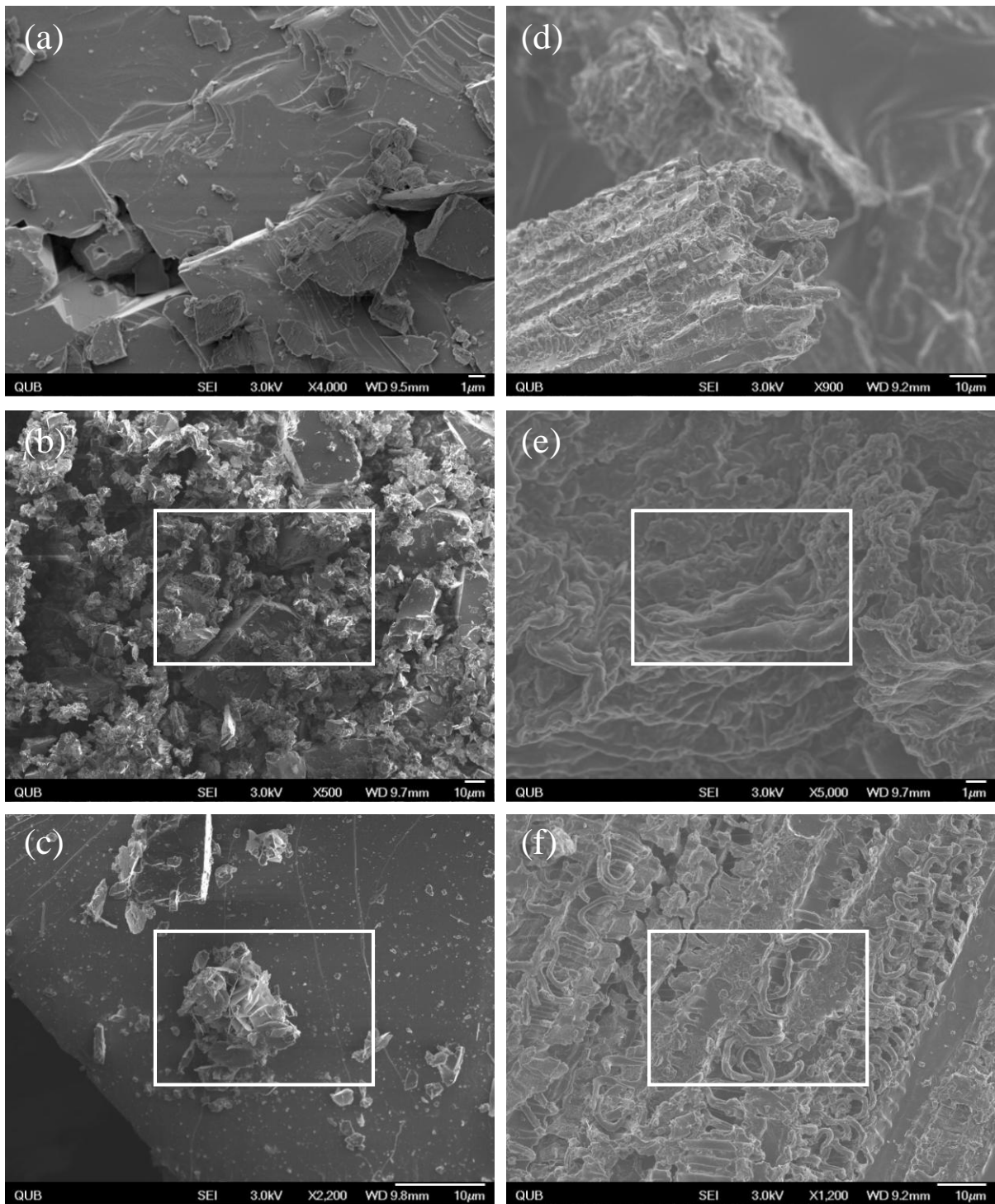


Figure 5: SEM images of Dolomite and Tea Waste before adsorption experiments (a) and (d), after Cu adsorption (b) and (e) and after MB adsorption (c) and (f) respectively.

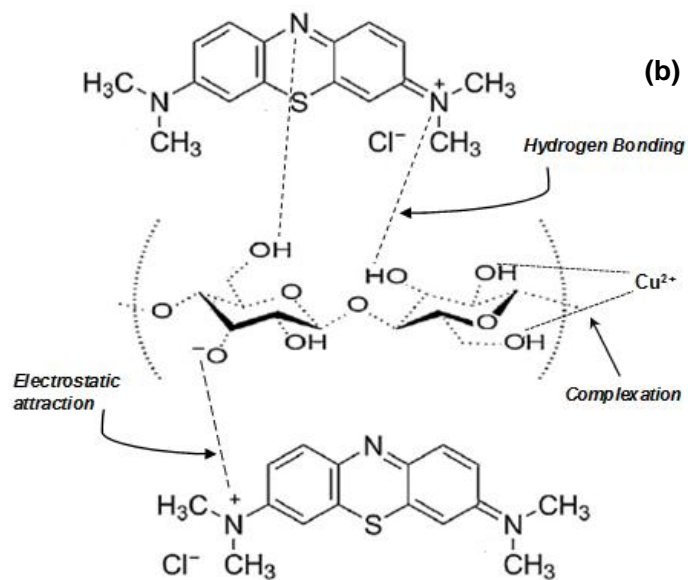
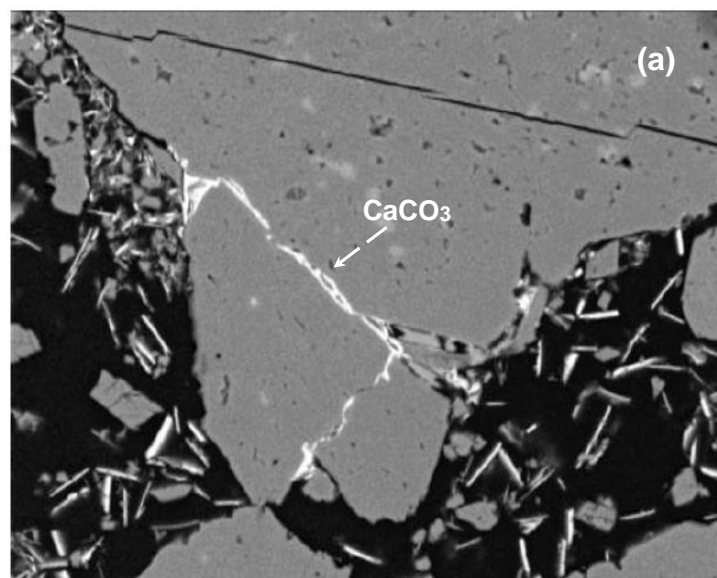


Figure 6: (a) Copper surface precipitation within cracks on dolomite (After Ref [25]) and (b) Metal ions and dye molecule removal through electrostatic attraction and hydrogen bonding (After Ref [45]).

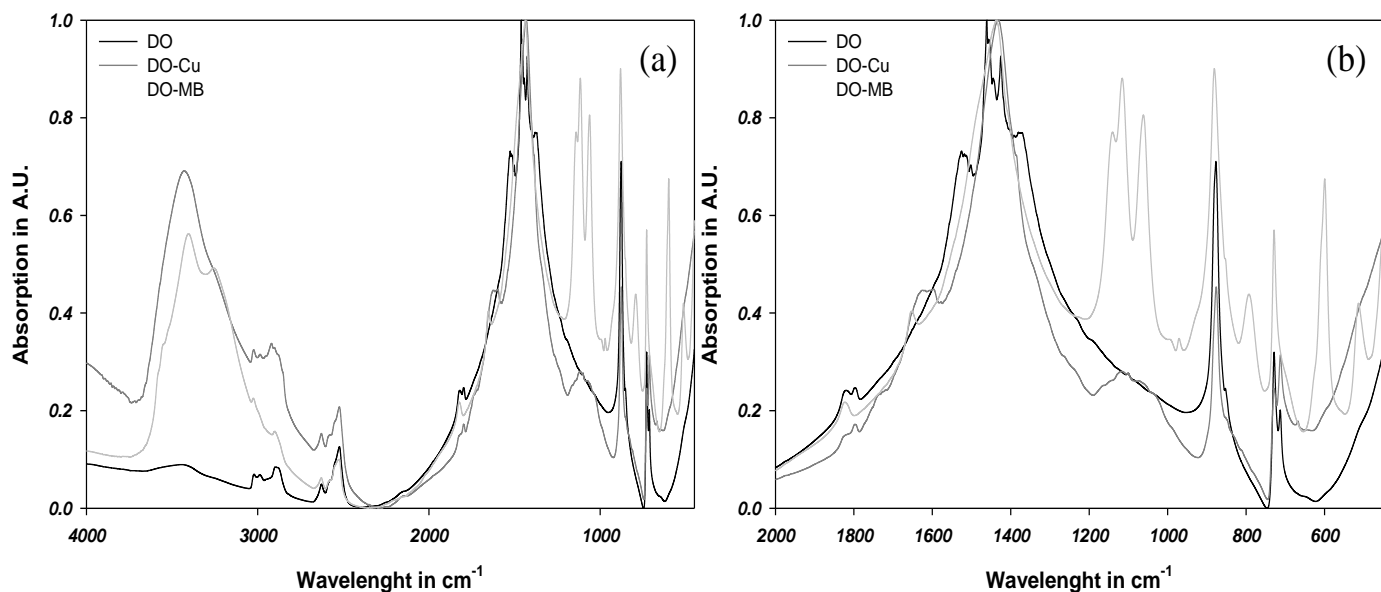


Figure 7: FTIR spectra of DO before and after adsorption with Cu and MB, (a) full spectrum and (b) close up onto the 2000 to 450 cm^{-1} region. The spectra are normalised and un-shifted.

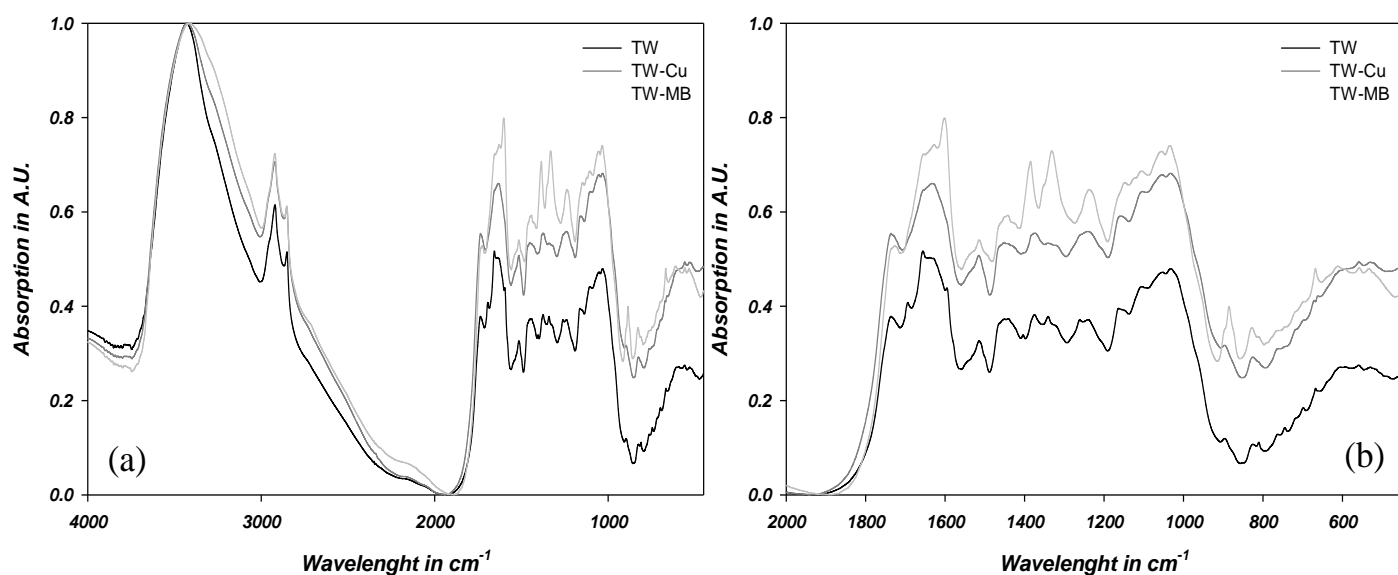


Figure 8: FTIR spectra of TW before and after adsorption with Cu and MB, (a) full spectrum and (b) close up onto the 2000 to 450 cm^{-1} region. The spectra are normalised and un-shifted.

Supplementary Material

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